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Application of a Swept-Potential Electrochemical Detector in the Liquid-Chromatographic Determination of Nitrosamines

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A swept-potential detector, operating in the square-wave voltammetric mode, is used in the liquid-chromatographic determination of a mixture of eight nitrosamines. Only three compounds were completely separated by the C-18 column. Three more were resolved by educing constant-potential chromatograms from the computer buffer. Mathematical deconvolution via fast-Fourier transform was applied to the remaining components.

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Short Communication

APPLICATION OF A SWEPT-POTENTIAL ELECTROCHEMICAL DETECTOR IN THE LIQUID-CHROMATOGRAPHIC DETERMINATION OF NITROSAMINES

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Summary. A swept-potential detector, operating in the square-wave voltammetric mode, is used in the liquid-chromatographic determination of a mixture of eight nitrosamines. Only three compounds were completely separated by the C-18 column. Three more were resolved by educing constant-potential chromatograms from the computer buffer. Mathematical deconvolution via fast-Fourier transform was applied to the remaining components.

In recent years, several publications have reported on the determination of nitrosamines [1—9]. The interest in nitrosamines stems from their carcinogenic nature and wide distribution as discussed by Samuelsson and Osteryoung [1] and by Vohra [2]. Several papers have dealt with the polarographic determination of nitrosamines [3—7]. Unfortunately, although modern polarographic methods are quite sensitive, they are not capable of the determination of most mixtures without a prior separation step, and the usual polarographic procedures are not suitable for volatile compounds because of the necessity for the removal of oxygen from the system. Analytical methods need to be applicable to mixtures of volatile and involatile nitrosamines, and to this end, several papers have advocated high-performance liquid chromatography (h.p.l.c.) with electrochemical detection [1, 2, 8, 9].

Most applications of h.p.l.c. entail the complete resolution of the components of the mixture by the column while the detector serves only to quantify each component. However, newer techniques rely on the detector to help identify the components and even to help resolve two or more components that are not completely resolved by the column. Outstanding examples are the multiwavelength ultraviolet (u.v.) detector [10] and the use of a mass spectrometer as a detector [11]. An analogous detector is the swept-potential electrochemical detector, first reported and applied to a mixture of two nitrosamines by Samuelsson et al. [12]. Reardon et al. [13] recently described improved instrumentation for swept-potential detection, and this communication describes the application of this new instrument to a mixture of nitrosamines in which the chromatographic peaks of several components overlap.

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Experimental

The h.p.l.c. system and swept-potential detector used in this study have been described [13—15]. The only significant changes from the previous work were the use of a Zorbax-ODS 4.6 X 150-mm column (DuPont Instruments) and the use of a methanol bubbler between the helium tank and the gas-dispersion tube in the mobile-phase reservoir to minimize changes of mobile-phase composition during a series of chromatograms.

The nitrosamines studied are listed in Table 1. These compounds (Sigma Chemical Company) were used without further purification. Because of the possible carcinogenic effects of *N*-nitroso compounds, they were ordered in serum bottles with septum caps. Stock solutions were prepared by injecting 50.0 ml of h.p.l.c.-grade methanol into the serum bottles. These stock solutions were diluted further in volumetric flasks to obtain sample solutions suitable for injection. All sample solutions were stored in the dark.

Mobile phases consisted of 0.20 M acetate buffers of various pH values, h.p.l.c.-grade methanol (Fisher), and 1-heptane sulfonic acid sodium salt (Eastman Kodak) as ion-pairing agent. The mobile phases were prepared as before [15] except for the addition of the ion-pairing agent.

Results and discussion

Figure 1 is a chromatogram of the eight nitrosamines listed in Table 1. This chromatogram was produced by summing the 21 difference measurements obtained in each square-wave voltammetric sweep and is similar to what would be observed with a d.c. electrochemical detector set to the potential of the negative limit of the sweep. The peaks for NDIPLA and NDM are not completely separated. In addition, the peaks for NMA, NDP, and NBE are fused into one asymmetric peak. The peaks for NDE, NBP, and

TABLE 1

Voltammetric peak potentials and chromatographic capacity factors

Compound	Abbreviated name	Peak potential[a]	Capacity factor[b]
N-Nitrosodiisopropanolamine	NDIPLA	−1.06	0.31
N-Nitrosodimethylamine	NDM	−1.14	0.41
N-Nitrosodiethylamine	NDE	−1.06	1.13
N-Nitroso-*N*-methylaniline	NMA	−0.84	3.68
N-Nitroso-di-n-propylamine	NDP	−1.04	3.87
N-Nitroso-*N*-ethylbutylamine	NBE	−1.04	4.15
N-Nitroso-*N*-butylpropylamine	NBP	−1.04	7.63
N-Nitrosodibutylamine	NDB	−1.02	15.58
Oxygen		−1.08	1.73

[a]Potentials were measured vs. Ag/AgCl in equal-volume mixtures of methanol and 0.02 M acetate buffer. Final pH was 5.55. [b]Capacity factors on Zorbax-ODS 4.6 x 150 mm column with mobile phase (note a) at 1.1 ml min^{-1}.

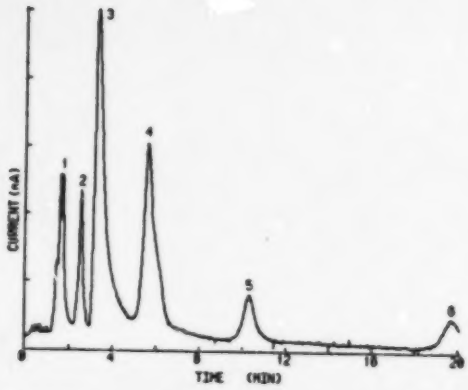

Fig. 1. Chromatogram of a mixture of nitrosamines. Peaks: (1) NDIPLA and NDM; (2) NDE; (3) oxygen; (4) NMA, NDP, and NBE; (5) NBP; (6) NDB. Currents summed over potential range of −0.80 to −1.22 V vs. Ag/AgCl. Injection of 10 μl containing 174 ng of each nitrosamine. See notes to Table 1 for composition of mobile phase. Voltammetric parameters: pulse, −50 mV; step, −20 mV; frequency, 30 Hz. Voltammograms of 21 points repeated once each second.

NDB are well separated. At lower percentages of methanol in the mobile phase, the peak from oxygen in the injected sample overlaps with the peak of NDE because the capacity factor for oxygen increases less than that for NDE. It was decided not to purge the sample solution with helium to remove the oxygen because of the volatility of the lower-molecular-weight nitrosamines. No significant changes in selectivity factors resulted from moderate changes in mobile-phase pH or from the addition of heptane sulfonic acid up to 2 mm in the mobile phase.

Figure 2 is a 3-D representation of a section of the complete run. The variations of reduction potentials are obvious and suggest approaches to resolving the two areas of overlapping peaks. The resolution of the NDIPLA/NDM doublet is greatly enhanced by the use of constant-potential chromatograms as shown in Fig. 3. Such chromatograms are constructed by educing one difference-current measurement from each sweep with each measurement corresponding to the same base potential. Figure 3 also shows clearly two unknown impurities which follow the solvent front very closely.

The use of constant-potential chromatograms also allows the complete resolution of the peak of NMA from the overlapping peaks of NDP and NBE as seen in Fig. 4, curve D. Unfortunately, NDP and NBE are so similar in reduction potential that constant-potential chromatograms cannot resolve them.

Mathematical deconvolution was applied to the NMA/NDP/NBE triplet starting with the raw data of Fig. 4, curve B, using the same microprocessor as for instrument control and data acquisition. An interpolated baseline was subtracted to produce the data of Fig. 5, curve A. Next, the data were

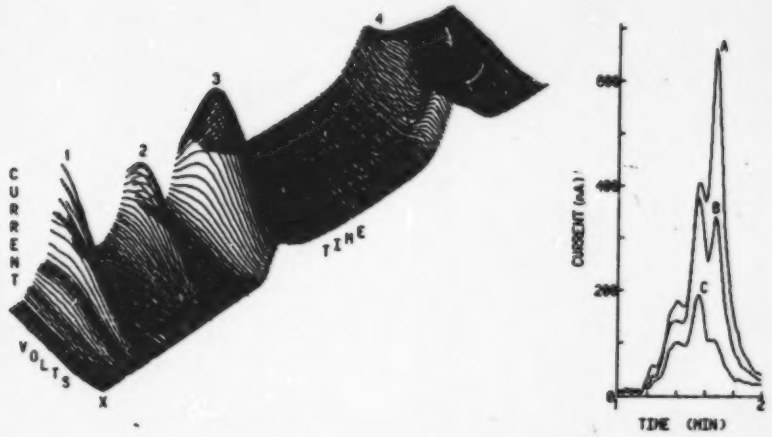

Fig. 2. 3-D chromatogram of a section of experiment depicted in Fig. 1. The time axis shows retention times from 1.0 to 6.7 min. Potential axis is from −0.80 to −1.22 V vs. Ag/AgCl. Origin (X) is 1.0 min and −0.80 V.

Fig. 3. Chromatograms at constant base potentials. Data are from the same experiment as Figs. 1 and 2, peak 1. Potentials of curves vs. Ag/AgCl: (A) −1.22 V; (B) −1.10 V; (C) −0.98 V.

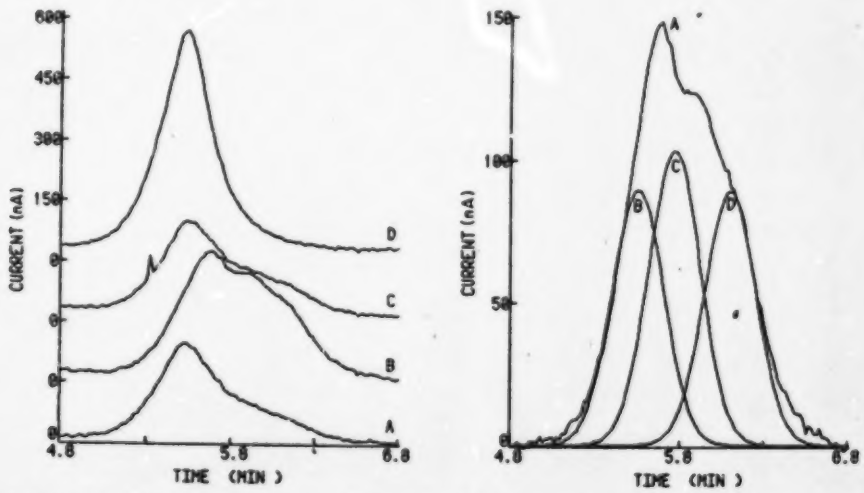

Fig. 4. Chromatograms at constant base potentials. Data are from the same experiment as Figs. 1 and 2, peak 4. Potentials of curves vs. Ag/AgCl: (A) −1.22 V; (B) −1.10 V; (C) −0.98 V; (D) −0.86 V.

Fig. 5. Deconvolution of curve B, Fig. 4. Curve A, baseline-subtracted experimental data. Curves B–D, deconvoluted peaks for NMA, NDP, and NBE, respectively. See text for details.

digitally filtered to remove high-frequency noise. A cutoff criterion described by Isenhour and Lam [16] was used for the fast Fourier-transform smoothing. Finally, an extension of the parameter estimation analysis of Binkley and Dessy [17] was used to perform the curve deconvolution on the assumption of three Gaussian peaks with the same half-height width. The linear parameter estimation was performed in the spatial frequency domain, by the least-squares method, after input of preliminary estimates of peak positions, peak width, and peak heights. The iterative calculation first optimizes the peak positions and then the peak width, using the minimum of residuals as the criterion of best fit. Finally, the peak heights are calculated in a similar manner. The resulting components are illustrated in Fig. 5, curves B—D. The retention time for curve B (NMA) is within one second of the retention time measured from Fig. 4, curve D.

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